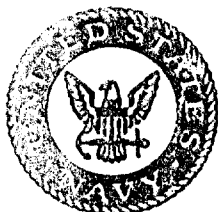


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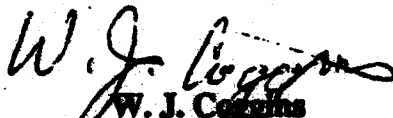
PREFACE


This document was prepared under the auspices of the NUWC FY92 Bid and Proposal Program.

The technical reviewer for this report was Mark Moffett (Code 3111).

The authors gratefully acknowledge the contributions of J. Lindberg and J. Powers (Code 2131) for helpful advice, T. Ramotowski (Code 2131) for technical and laboratory expertise, K. Janeczek (Code 2131) for fabrication techniques, and C. Wyatt (Code 2132) for measurement expertise.

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REPORT DOCUMENTATION PAGEForm Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave Blank)		2. REPORT DATE 31 March 1994	3. REPORT TYPE AND DATES COVERED Final
4. TITLE AND SUBTITLE Development of a High-Frequency Multilayer Copolymer Acoustic Projector			5. FUNDING NUMBERS PR A10016
6. AUTHOR(S) George J. Kavarnos and Elizabeth A. McLaughlin			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Undersea Warfare Center Detachment 39 Smith Street New London, Connecticut 06320-5594			8. PERFORMING ORGANIZATION REPORT NUMBER TD 10,607
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Naval Undersea Warfare Center Division 1176 Howell Street Newport, Rhode Island 02841-1708			10. SPONSORING/MONITORING AGENCY REPORT NUMBER
11. SUPPLEMENTARY NOTES			
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited.			12b. DISTRIBUTION CODE
13. ABSTRACT (Maximum 200 words) This report describes the preparation of piezoelectric vinylidene fluoride-trifluoroethylene [P(VDF-TrFE)] copolymer films for a broadband, high-frequency projector, and the fabrication and acoustic testing of the projector. Raw P(VDF-TrFE) copolymer powder was dissolved in an organic solvent and cast into a shallow mold. After the solvent had evaporated, the ~200 μm thick films were annealed and subsequently slow cooled. A gold/palladium metallic layer was sputtered onto both sides of the film for electrodes, and each film was conventionally poled in a hot oil bath. The capacitance of a single layer with an area of 6.45 cm^2 (1 in.^2) was typically ~200 pF. The electroded copolymer layers were bonded together with epoxy and wired in parallel. The piezoelectric constant d_{33} measured on a four-layer sample, using laser Doppler vibrometry, was -34 pC/N. A seven-layer sample was waterproofed and the projector was evaluated acoustically. The transmitting voltage response at resonance (542 kHz) was 156 dB/ $\mu\text{Pa-m/V}$, and the bandwidth was 240 kHz.			
14. SUBJECT TERMS Copolymer Films Multilayer Copolymer Acoustic Projector			15. NUMBER OF PAGES 22
			16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT SAR

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LIST OF SYMBOLS

A	area (m^2)
b	beam pattern parameter
C	capacitance (F)
c	speed of sound in the medium (m/s)
c_{33}^E	constant electric field stiffness coefficient of a material (Pa)
DI	directivity index
DSC	differential scanning calorimetry
d_{33}	piezoelectric strain constant (C/N)
E	maximum drive field (V/m)
ϵ	relative permittivity
ϵ_{33}^T	constant stress permittivity (F/m)
F	orientation coefficient
FOM	figure of merit
FTIR	Fourier transform infrared spectroscopy
f	frequency (Hz)
f_0	resonance frequency (Hz)
G	input electrical conductance (mmhos)
η	efficiency (%)
k	wavenumber (1/m)
k_{33}	coupling factor
L	length of the side of the transducer (m)
L_0	local-field coefficient
MEK	methyl ethyl ketone
P_r	remanent polarization (C/m ²)
P_s	saturation polarization (C/m ²)
PVDF	poly(vinylidene fluoride)
P(VDF-TrFE)	poly(vinylidene fluoride-trifluoroethylene)
PZT-4	lead zirconate titanate
Q	electroacoustic quality factor
ρ	density of material (kg/m ³)
s_{33}^E	constant field compliance coefficient (1/Young's Modulus) (m ² /N)
s_{33}^a	compliance coefficient for the amorphous region of a semicrystalline material (m ² /N)
s_{33}^c	compliance coefficient for a pure crystal (m ² /N)
s_{33}^s	compliance coefficient for a semicrystalline material (m ² /N)
S_{max}	maximum strain
t	thickness of the material (m)
T_c	Curie transition temperature (°C)
T_m	melting point temperature (°C)
TrFE	trifluoroethylene
TVR	transmitting voltage response (dB//1 μ Pa-m/V)
θ	spatial angle of beam pattern (degrees)
v_{33}^E	speed of sound in a material with a constant electric field (m/s)
VDF	vinylidene fluoride
X_c	degree of crystallinity

DEVELOPMENT OF A HIGH-FREQUENCY MULTILAYER COPOLYMER ACOUSTIC PROJECTOR

INTRODUCTION

The goal of this project was to investigate the feasibility of using piezoelectric fluoropolymer as the active material in a 6.45 cm² (1 in.²) high-frequency, broadband projector. Poly(vinylidene fluoride) homopolymer, PVDF, and its copolymer with trifluoroethylene, P(VDF-TrFE), are among the best candidates of fluoropolymers which satisfy the Navy requirements for light-weight, thin, and low-cost underwater sonar projectors. Since they possess impedances similar to that of water, these materials are acoustically transparent over a large frequency range and, accordingly, have a broadband transmitting response. PVDF is prepared from a single monomer unit of vinylidene fluoride, VDF. P(VDF-TrFE) consists of monomer units of vinylidene fluoride and trifluoroethylene, TrFE, randomly linked together. Several compositions of P(VDF-TrFE) are currently available with VDF ranging from about 50 mol% to over 90 mol%. The salient chemical compositional distinction between PVDF and P(VDF-TrFE) is that they differ in fluorine content with PVDF having the lowest fluorine content and 50 mol% P(VDF-TrFE) having the highest. PVDF and P(VDF-TrFE) can be obtained as unprocessed, nonpiezoelectric powders, or as finished piezoelectric products.

For many sonar applications, P(VDF-TrFE) copolymers possess a distinct advantage over PVDF in that the latter requires mechanical stretching prior to poling, adding significantly to fabrication costs. However, since P(VDF-TrFE) can be poled without stretching, the copolymer can be solvent cast or injection molded into a desired geometry prior to poling. Processing conditions for the copolymers are, therefore, simpler and less costly.

Typically, polymers are used in a thickness mode where a flat sheet is poled in a direction normal to its surface. For a lower frequency operation, a thick polymer is required. However, a thick polymer layer requires unreasonably large voltages to polarize. It is, therefore, desirable to use multiple thin layers of the piezoelectric copolymer, each layer poled with a lower voltage. The layers are stacked and wired in parallel to keep the drive voltage manageable (100 V).

THEORY

MATERIAL CONSIDERATIONS

P(VDF-TrFE) copolymer is available as a powder in various compositions differing in the relative amounts of VDF and TrFE. The most suitable compositions for underwater piezoelectric applications are those with VDF levels between 70% and 80%, as has been shown by a molecular modeling simulation performed in this laboratory.¹ This work has demonstrated that these compositions possess the required polarization for piezoelectric applications. The polarization behavior of these materials is due to the polar nature of the crystalline β phase. The remanent polarization, P_r , i. e., the residual

polarization after taking into account the degree of crystallinity, local field, and copolymer orientation, can be estimated from $P_r = X_c F L_s P_s$, where P_s is the saturation polarization of the copolymer crystal unit cell arising from the sum of all carbon-fluorine dipoles.^{2,3} X_c is the degree of crystallinity, F is the orientation coefficient, which is a measure of the alignment of the copolymer crystals with respect to the plane of the film, and L_s is the local-field coefficient. Since copolymer compositions are well aligned along the c axis parallel to the plane of the film, a value of 0.9 for F is usually assumed. The local field refers to the polarization on the surface of a spherical cavity surrounding the dipole. For PVDF, L_s can be assumed to be unity.³ In agreement with this, Al-Jishi and Taylor found a negligible reduction in the polarization due to the local field, using a model of extended dipoles.^{4,5} In the case of P(VDF-TrFE) copolymer, the remanent polarization is enhanced due to favorable intermolecular and intramolecular dipole-dipole interactions.⁶

When a piezoelectric polymer is placed in an electric field, the material undergoes a strain. The d_{33} coefficient, which relates the resulting strain on application of an electric field in the poling direction, can be written as

$$d_{33} = -P_r s_{33}^E, \quad (1)$$

where s_{33}^E is the compliance coefficient for a constant electric field (the reciprocal of the Young's modulus). The k_{33} coupling factor, which is the fraction of electrical energy converted to mechanical energy (or the reverse), can be calculated from

$$k_{33}^2 = P_r^2 \frac{s_{33}^E}{\epsilon_{33}^T}, \quad (2)$$

where ϵ_{33}^T is the permittivity for constant stress. The material and acoustic properties of traditional PZT-4, PVDF, and 75 mol% P(VDF-TrFE) are listed in table 1. The polarizations of the fluoropolymers were calculated from the dipole moments of the polymer crystallites using molecular modeling and crystal packing techniques developed at NUWC.⁷ Corrections for local field effects were applied to the polarizations.⁸ The d_{33} and k_{33} values of 75 mol% P(VDF-TrFE) were then calculated by substituting the experimental s_{33}^E values into equations (1) and (2), respectively.

The energy density listed in the fifth column of table 1 is the figure of merit (FOM) of the transducer material. The FOM is written as

$$FOM = \frac{1}{2} \frac{S_{max}^2}{s_{33}^E}, \quad (3)$$

where S_{max} is the maximum strain given by

$$S_{max} = E d_{33}. \quad (4)$$

E is the maximum applied drive field. Table 1 shows that high moduli and polarizations result in large FOMs. Since P(VDF-TrFE) copolymer can vary in degree of crystallinity, s_{33}^E and FOM can vary depending on processing and annealing conditions. To estimate the FOM of copolymer with a different degree of crystallinity, it is desirable to have a way of determining the effect of X_c on the compliance. Molecular mechanics calculations suggest that crystallites of PVDF and copolymer have much lower compliances than those of semicrystalline polymer. The compliance of the amorphous region, s_{33}^a , of a semicrystalline polymer whose compliance, s_{33}^{sc} , and degree of crystallinity are known can be calculated from⁸

$$s_{33}^a = \frac{s_{33}^{sc} - X_c s_{33}^c}{(1 - X_c)} \quad (5)$$

The calculated value of s_{33}^a can then be used to estimate s_{33}^{sc} of a polymer with a different degree of crystallinity. For example, the compliance coefficient of a pure crystal of 75 mol% P(VDF-TrFE) has been calculated to be $s_{33}^c = 3.97 \times 10^{-11} \text{ m}^2/\text{N}$. Given that s_{33}^{sc} for semicrystalline 75 mol% P(VDF-TrFE) where $X_c \sim 0.75$ has been measured to be $30 \times 10^{-11} \text{ m}^2/\text{N}$,⁹ it is estimated that $s_{33}^a \sim 1.25 \times 10^{-9} \text{ m}^2/\text{N}$. Using the latter value, P(VDF-TrFE) copolymer annealed sufficiently long to give a crystallinity of 90% is predicted to have a modulus of $s_{33}^{sc} \sim 1.4 \times 10^{-10} \text{ m}^2/\text{N}$. This translates into a FOM of 2770 J/m^3 . Thus, although the dielectric loss of polymer is greater than that of PZT-4 and the drive voltages required to excite the polymer are about 50 times larger than those for ceramic, the potentially high FOM's of copolymers and their acoustic transparency suggest that these materials may be useful candidates for certain sonar projector applications.

Another factor to consider in selecting P(VDF-TrFE) copolymer composition is the Curie transition temperature, T_c , which signals the crystal-crystal transition between the lower temperature, ordered ferroelectric phase and the higher temperature, disordered paraelectric phase. It is the ferroelectric phase that can be made piezoelectric. In transducer applications, it is desirable to maintain the temperature of the piezoelectric polymer below the Curie temperature to prevent the polymer from losing its polarization. When exposed to temperatures greater than T_c , piezoelectric polymers depolarize by thermally-induced transformations within the crystalline phase. For example, figure 1 shows that T_c of unannealed P(VDF-TrFE) copolymer falls as the VDF content decreases. It is evident that copolymers with VDF < 60% may not be suitable for transducer applications where temperature stability is required. To avoid the possibility of depoling at higher temperatures, copolymer with 75 mol% P(VDF-TrFE) was considered as the most suitable copolymer composition for this project. A pilot study carried out in this laboratory revealed that T_c of annealed copolymer with this composition is $\sim 125^\circ\text{C}$.

PROJECTOR DESIGN CONSIDERATIONS

A projector design that demonstrates the performance of the proposed piezoelectric copolymer can be modeled as a half-wave resonator operating in the thickness mode. The projector may consist of numerous layers of piezoelectric material interspersed with electrodes. In selecting the dimensions and number of layers, there are several issues to consider. First, there must be a sufficient thickness to reduce the resonance frequency to a range where measurements may more easily be performed, but a large number of layers would involve extensive wiring and fabrication problems. It was, therefore, decided to limit the number of layers of the prototype device to seven.

The resonance frequency, f_0 , assuming a constant electric field in each layer, can be estimated as

$$f_0 = \frac{v_{33}^E}{2t}, \quad (6)$$

where

$$v_{33}^E = \sqrt{\frac{c_{33}^E}{\rho}}. \quad (7)$$

v_{33}^E is the speed of sound in the material, t is its thickness, c_{33}^E is the stiffness coefficient for constant electric field, and ρ is the density of the material.¹⁰ We used equations (6) and (7) to calculate a resonance frequency for a thin film of polymer. Assuming that the density of P(VDF-TrFE) copolymer is 1.9 g/cm³ (1900 kg/m³), its thickness 200 μ m, and its stiffness coefficient 7 GPa, we obtained a value of $f_0 \approx 5$ MHz. This value was above the range of what could accurately be measured with the available equipment. However, by stacking seven layers of 200 μ m thick polymer, we reduced the calculated resonance frequency to ~ 700 kHz. When the polymer layers are bonded together with metal electroding material, the resonance frequency is expected to be below 700 kHz because of increased thickness and mass.

POLYMER PROCESSING AND PROJECTOR FABRICATION

PROCESSING PIEZOELECTRIC P(VDF-TrFE) COPOLYMER FILM

The preparation of a piezoelectric copolymer film requires several steps: solvent casting, annealing, electroding, and electric poling.

Solvent-Casting

At the outset of this project, several experiments were performed to establish the optimum conditions to solvent cast the copolymer into 100 μ m thick layers. Typically, 20 grams of 75 mol% VDF copolymer powder were dissolved in 100 milliliters of methyl ethyl ketone (MEK). A 0.127 m x 0.127 m x 0.127 mm (5 in. x 5 in. x 0.005 in.) mold was cut out of a Teflon block (figure 2) and placed on a level surface. After pouring the polymer solution into the mold, the MEK solvent was slowly evaporated under a reduced vacuum for several days. A Fourier transform infrared spectroscopic (FTIR) study was carried out to determine the time required to drive off the solvent completely since any residual MEK remaining in the cast films can adversely affect performance in an acoustic projector.¹¹ For example, residual organic solvent remaining in P(VDF-TrFE) copolymer may lead to an undesirable increase in its compliance. The infrared transmittance of the solvent cast film was recorded from 4000 cm⁻¹ to 400 cm⁻¹ (figure 3). In this region there appears a sharp band at 1712 cm⁻¹ due to C=O carbonyl

absorption of MEK, well separated from absorption bands of the polymer itself. Although MEK eventually disappears from the films after several weeks, annealing the films was sufficient to drive all of the residual MEK (the annealing procedure is described below). From the spectrum taken after annealing (figure 3), it is evident that the 1712 cm^{-1} peak disappears, indicating that all of the MEK has been evaporated off.

We used $200\text{ }\mu\text{m}$ thick P(VDF-TrFE) copolymer films to construct the copolymer projector. This layer thickness was thin enough so that reasonable poling and drive voltages would suffice yet not so thin that the bonding thickness would dominate the performance of the projector.

Annealing

The piezoelectricity of P(VDF-TrFE) copolymer films depends in part on the property of these materials to form platelet-like crystals (lamellae). Thick lamellar crystals are highly oriented. In fact, the formation of thick lamellae favors improved piezoelectric performance since the crystallites are polar and hard, as discussed in Material Considerations. To achieve thick lamella crystalites, the solvent-cast polymer must be annealed. Lamella thickness is inversely proportional to the degree of undercooling, which is defined as the difference between the crystallization temperature and the temperature of the solution. During crystallization from the melt or solution, the flexible polymer chains form lamella crystals by a chain-folding process. Crystallization occurs in the paraelectric phase, which is the nonferroelectric phase above the Curie transition. The presence of conformational defects guarantees that in the paraelectric phase the chains are well-separated and sufficiently mobile so that during crystallization they can undergo rearrangements to grow thick lamellar crystals.¹² These defects may consist of a random number of TG, TG', and TT (T = trans; G = gauche) bonds in the polymer chain.¹³ When the copolymer is annealed at an elevated temperature in the paraelectric phase just below the melting point, the polymer undergoes the slow molecular relaxations required for formation of thick lamella crystal. To further enhance the lamella thickness, the annealed copolymer is slow cooled to room temperature. During slow cooling, further molecular relaxations take place, favoring the growth of crystalline polymer. In summary, thick lamella crystals can be produced by annealing at small undercoolings followed by slow cooling.

Differential scanning calorimetry (DSC) was performed on the 75 mol% P(VDF-TrFE) copolymer composition before and after annealing (figure 4) to determine the Curie temperature (T_c) and the melting point of the copolymer (T_m). Annealing at a small undercooling temperature resulted in material having a high Curie transition temperature. For example, the T_c of copolymer annealed at 135°C is over 12°C higher than copolymer annealed at 125°C . The crystalline phase of copolymer annealed at small undercoolings is probably rich in VDF monomers and hence should have greater thermal stability than if annealed at a lower temperature. Annealing times of 2 hours at 135°C followed by slow coolings were found to be the minimum conditions for obtaining highly polarized film. Longer annealing times, e.g., one week, did not lead to any significant improvement in polarization. In fact, films annealed for long durations are brittle, inflexible, and slightly curved. These films were considered as unsuitable for a prototype multilayered projector that requires flat layers.

Electroding

Prior to the poling procedure, a thin layer of gold/palladium (Au/Pd) alloy ($\sim 0.150\text{ }\mu\text{m}$) was sputtered onto both sides of the annealed copolymer.¹⁴ A 6.4 mm margin from the edge of the polymer was maintained around the perimeter to avoid the possibility of electrical arcing during poling.

Poling

A fixture to hold the film in place was constructed from plexiglass (figure 5). The film was positioned between two brass electrodes that were connected to a high voltage DC power supply. After the electroded film was positioned in the fixture, the assembly was placed in a castor oil bath heated to 70°C and stirred slowly with a magnetic stirrer. The voltage was adjusted to achieve an electric field of 85 MV/m. Although polarization could be obtained within several minutes, the samples were routinely poled for 15 minutes at 70°C to guarantee maximum poling. The piezoelectric constants of poled electroded copolymer films were measured with a Berlincourt d_{33} meter.

FABRICATION OF A FOUR-LAYER RESONATOR AND SEVEN-LAYER PROJECTOR

Two resonator assemblies, each containing four layers of P(VDF-TrFE) copolymer, were fabricated for purposes of measuring the d_{33} coefficients. Subsequently, two seven-layer units were constructed to demonstrate the performance of copolymer material in an underwater projector.

The 200 μm thick poled copolymer sheets were carefully trimmed to 1 in. squares using a Dremel tool with a metal impregnated rubber wheel. Two 1 in. square aluminum plates were used to gently clamp each copolymer layer in a sandwich-like configuration during the trimming procedure. A stack of alternating layers of copolymer film and nickel mesh was bonded together with Miller-Stevenson 907 epoxy adhesive. The purpose of the mesh was to allow a convenient method of wiring the stack in parallel and to maintain bonds of constant thickness. The thickness of the nickel mesh was measured to be 50 μm . The metal layers were cut into 1 in. squares, each with a tab for wiring. A fixture was used to align the layers and to allow excess epoxy to escape while a pressure of 10 psi was applied. The epoxy cured overnight at about 45°C.

Figure 6 shows the four layer resonator. Figure 7 shows the seven layer underwater projector encapsulated in Hexcel® Uralite 3140 with an overall thickness of 6.4 mm (0.25 in.). The stack alone has a thickness of 1.8 mm (0.071 in.).

RESULTS AND DISCUSSION

The capacitances, C , and dissipation factors of the poled copolymer layers were measured at 1 kHz. These values were found to average about 200 pF and 0.018, respectively. The permittivities were calculated by the capacitance formula:

$$\epsilon = \frac{Ct}{A}, \quad (8)$$

where A is the area and t is the thickness of the dielectric.¹⁵ The averaged relative permittivity was 7.2. This is in close agreement with the value obtained by Ohigashi.¹⁶ The piezoelectric coefficients of individual layers averaged to $d_{33} = -23$ pC/N when measured with the Berlincourt meter. Using laser Doppler vibrometry on each of the four layer units,¹⁷ the average d_{33} for one unit was -33.5 pC/N

(standard deviation = 1.2) at measurements conducted at ten frequencies below 2 kHz and between 3 and 8 kHz. For the other unit, the d_{33} averaged to -23.6 pC/N (standard deviation = 0.88) for measurements between 1 and 7 kHz. The difference between the two d_{33} values is probably not due to instrumental error but rather to differences in the composite structures of each unit. For example, the first unit was constructed using a set of copolymer layers that had large d_{33} (Berlincourt) coefficients.

Transmitting voltage responses (TVR) and beam patterns of the two seven-layer devices were measured at the Naval Research Laboratory/Underwater Sound Reference Detachment calibration facility in Orlando, Florida.¹⁸ The TVR indicates the sound pressure at one meter per unit volt input. A representative TVR from 80 to 740 kHz of a seven-layer assembly taken at 22°C at a depth of 0.5 m (4.9 kPa) is shown in figure 8. The TVR peaks at 542 kHz with a value of 156 dB/μPa-m/V. The 3 dB down bandwidth is approximately 240 kHz. The electroacoustic quality factor, Q , is 2.3. The response of the projector was linear up to a drive level of 100 V, which was the limit of the equipment. The TVRs were used to estimate the electroacoustic efficiency, η_{ea} , which is defined as the percent of input electrical power converted to acoustical power:¹⁹

$$10\log\eta_{ea} = TVR - 170.9 - DI - 10\log G, \quad (9)$$

where DI is the directivity index, and G is the input electrical conductance in mhos. η_{ea} was estimated to be 12% for a frequency of 550 kHz, where the directivity index (DI) was calculated to be 27.4 dB, and G was measured to be 0.48 mmhos.

Beam patterns, taken at 200, 405, 540, and 680 kHz, are shown in figures 9 to 12. Using equations (10), (11), and (12), we can analyze these beam patterns using the parameter b ²⁰

$$b(\theta) = 20\log \left| \frac{\sin v}{v} \right|, \quad (10)$$

where

$$v = \frac{1}{2} kL \sin \theta, \quad (11)$$

and

$$k = \frac{2\pi f}{c}. \quad (12)$$

θ is the spatial angle of the beam pattern, c is the speed of sound in the medium, and L is the length of the side of the transducer. Using $c = 1500$ m/s and $L = 0.0254$ m, we calculated the 3 dB down width of the major lobe, 2θ , to be 5.54° for the beam pattern 540 kHz. This value agrees very well with the pattern shown in figure 11.

CONCLUSIONS

It has been shown that the nature of the thermal and crystallization conditions of unprocessed copolymer plays a key role in the development of high performance piezoelectric copolymer. These conditions have been defined for the 75 mol% P(VDF-TrFE). Annealing at 135°C for at least two hours and slow cooling to room temperature results in crystalline copolymer. Then poling at 70°C for 15 minutes in an electric field of 85 MV/m makes the copolymer piezoelectric.

Further experiments are now in progress to improve on the piezoelectric properties of the copolymer, to decrease the bond thickness, and to fabricate projectors with additional layers in an effort to lower the resonance frequency. In particular, we are exploring the feasibility of using low-temperature diffusion bonding as a means to bond together electroded copolymer layers. It is expected that thin bonding layers obtained using low-temperature diffusion bonding will reduce the influence of the bonding layer and improve the performance of the projector.

CURIE TRANSITIONS AND MELTING POINTS OF VF2 / EF3 COPOLYMERS

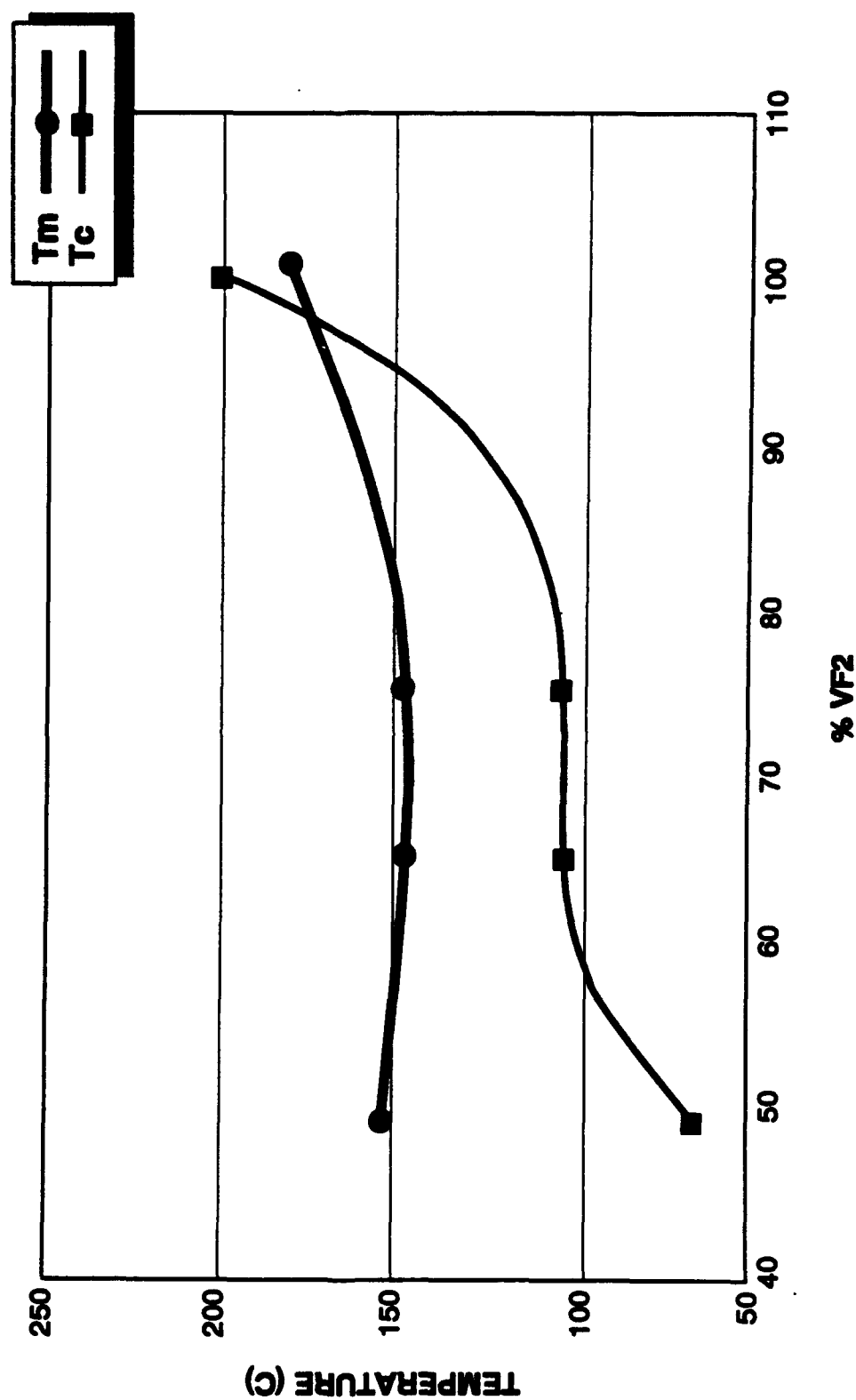


Figure 1. Effect of Fluorine Content on T_c and T_m of Unannealed P(VDF-TrFE)

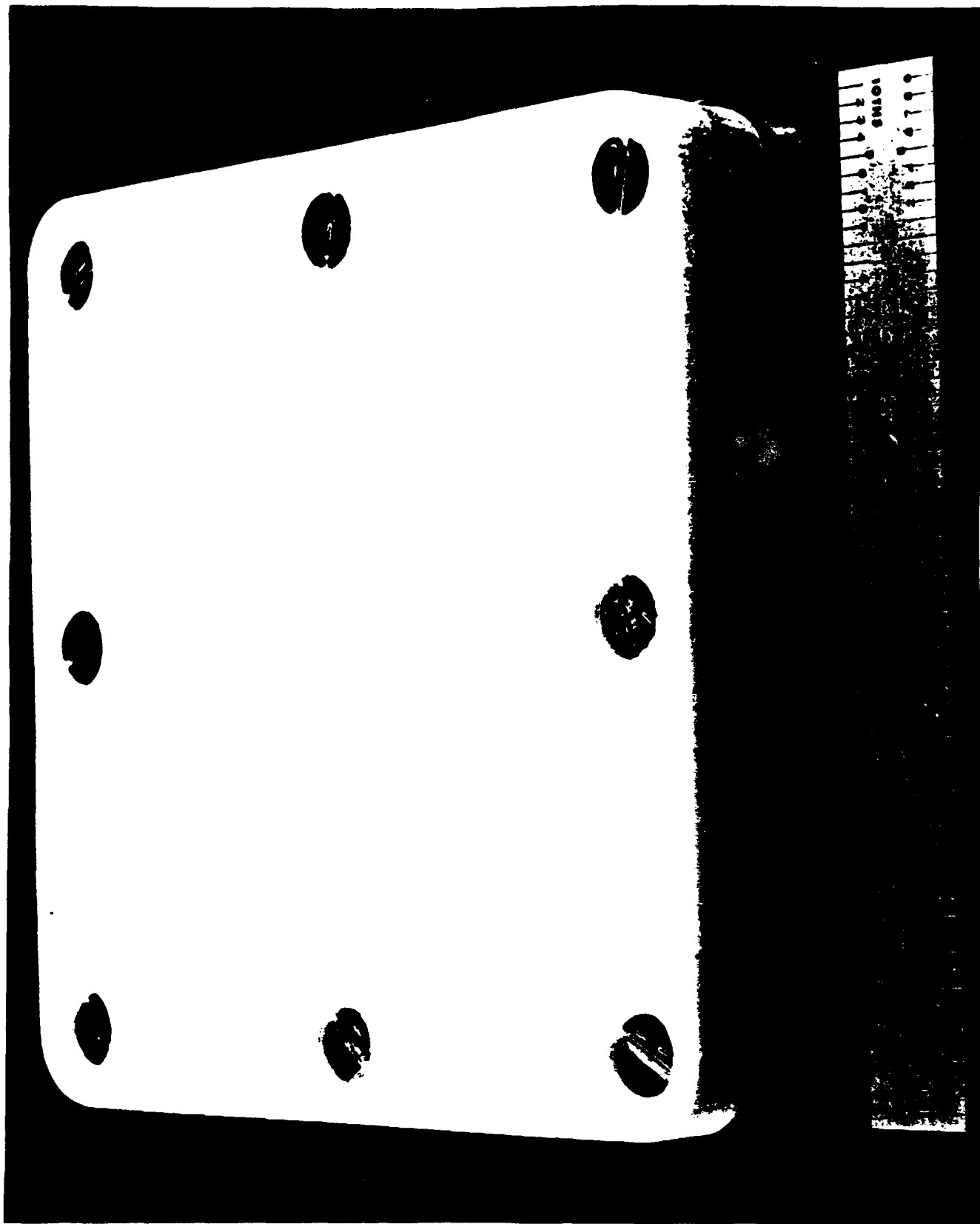


Figure 2. Teflon Mold Used to Cast MEK Solution of P(VDF-TrFE)

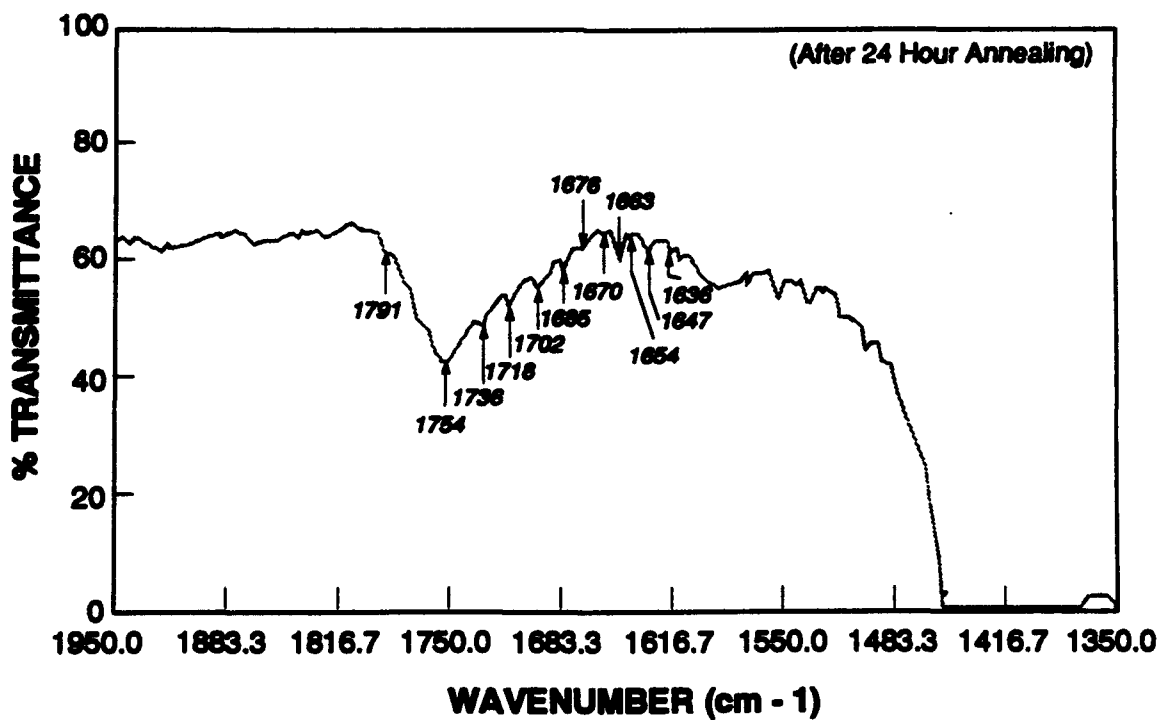
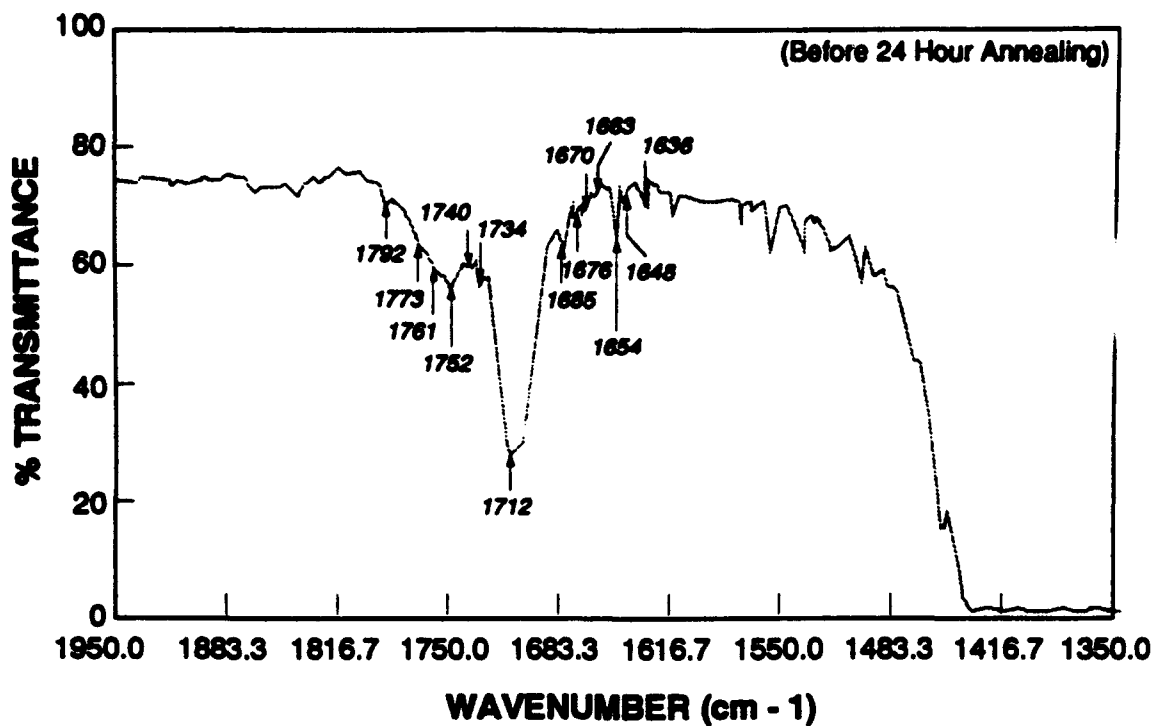


Figure 3. Infrared Spectra of Freshly Cast P(VDF-TrFE) Copolymer Film Before and After 24 Hour Annealing

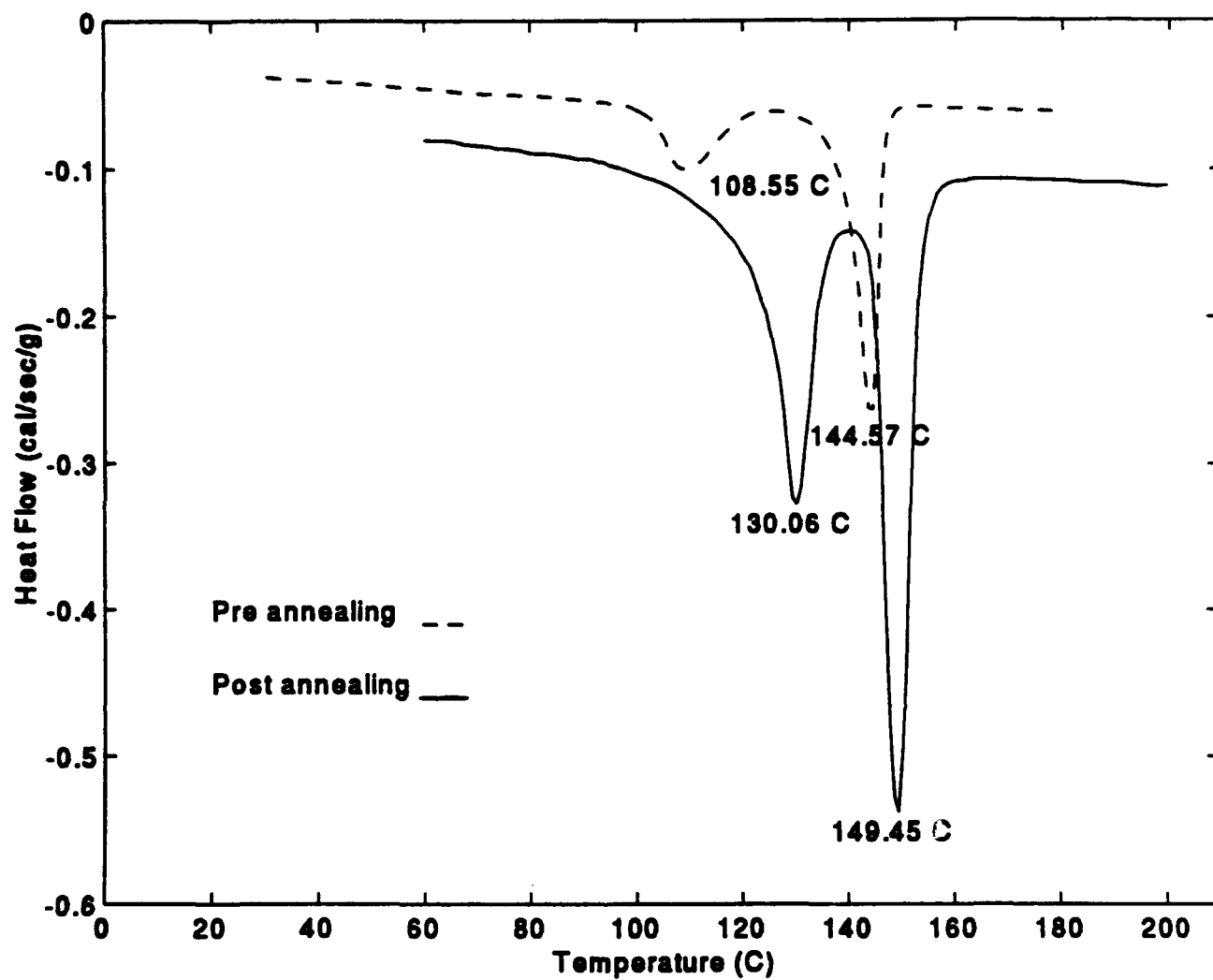


Figure 4. Differential Scanning Calorimetric Plots of P(VDF-TrFE) Copolymer Before and After Annealing at 135°C for Two Hours Followed by Slow Cooling

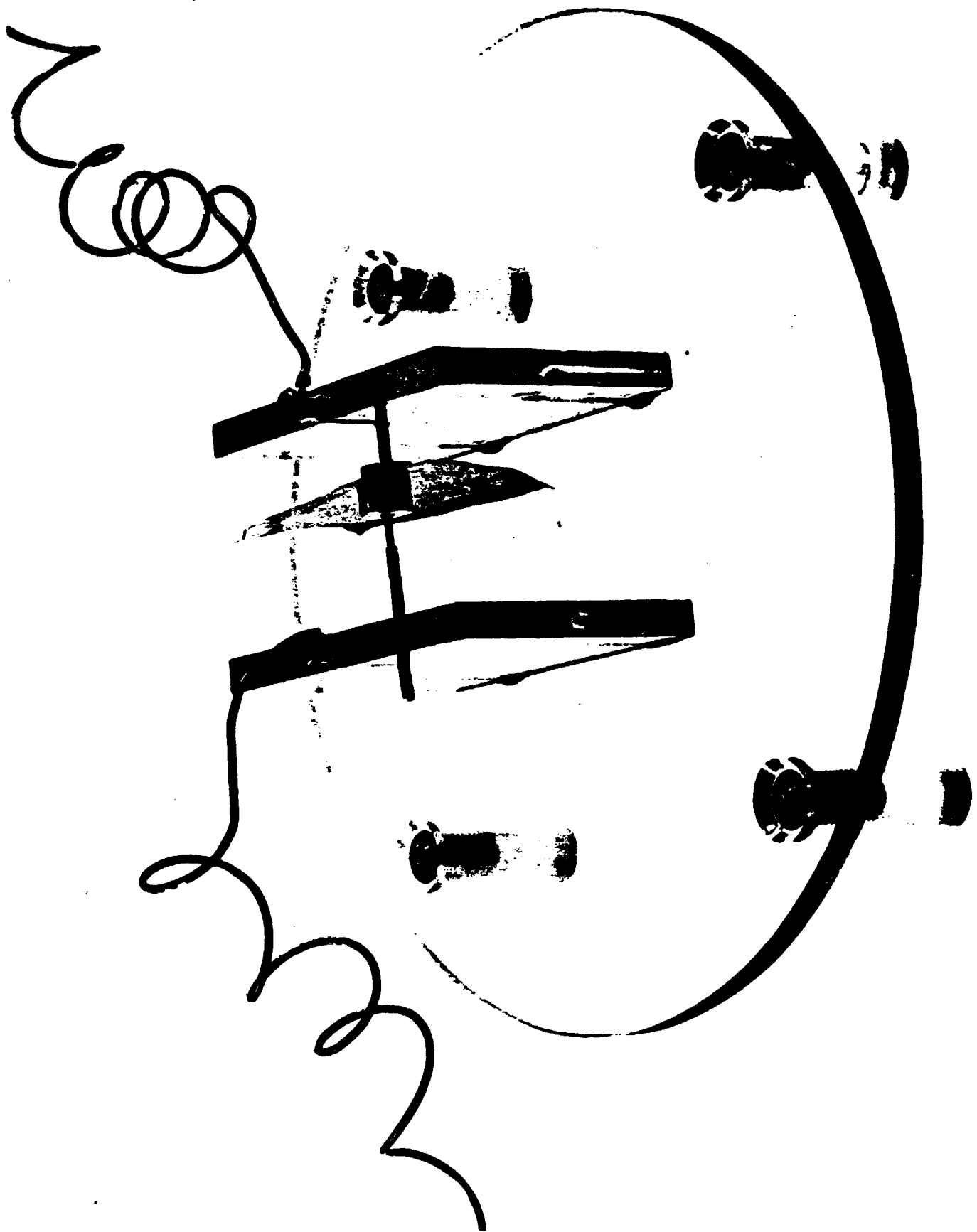


Figure 5. The Poling Fixture

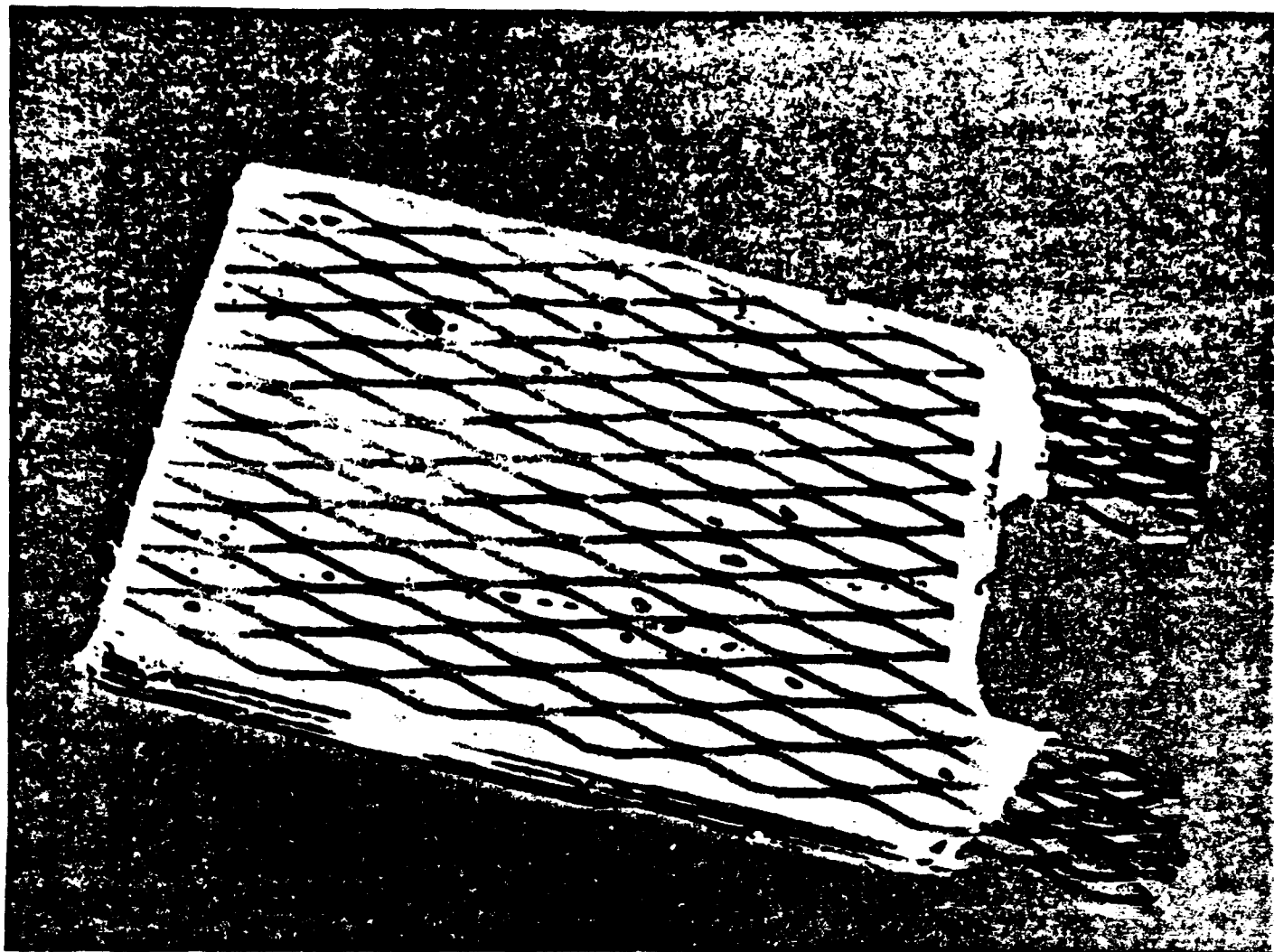


Figure 6. Four-Layer Copolymer Assembly

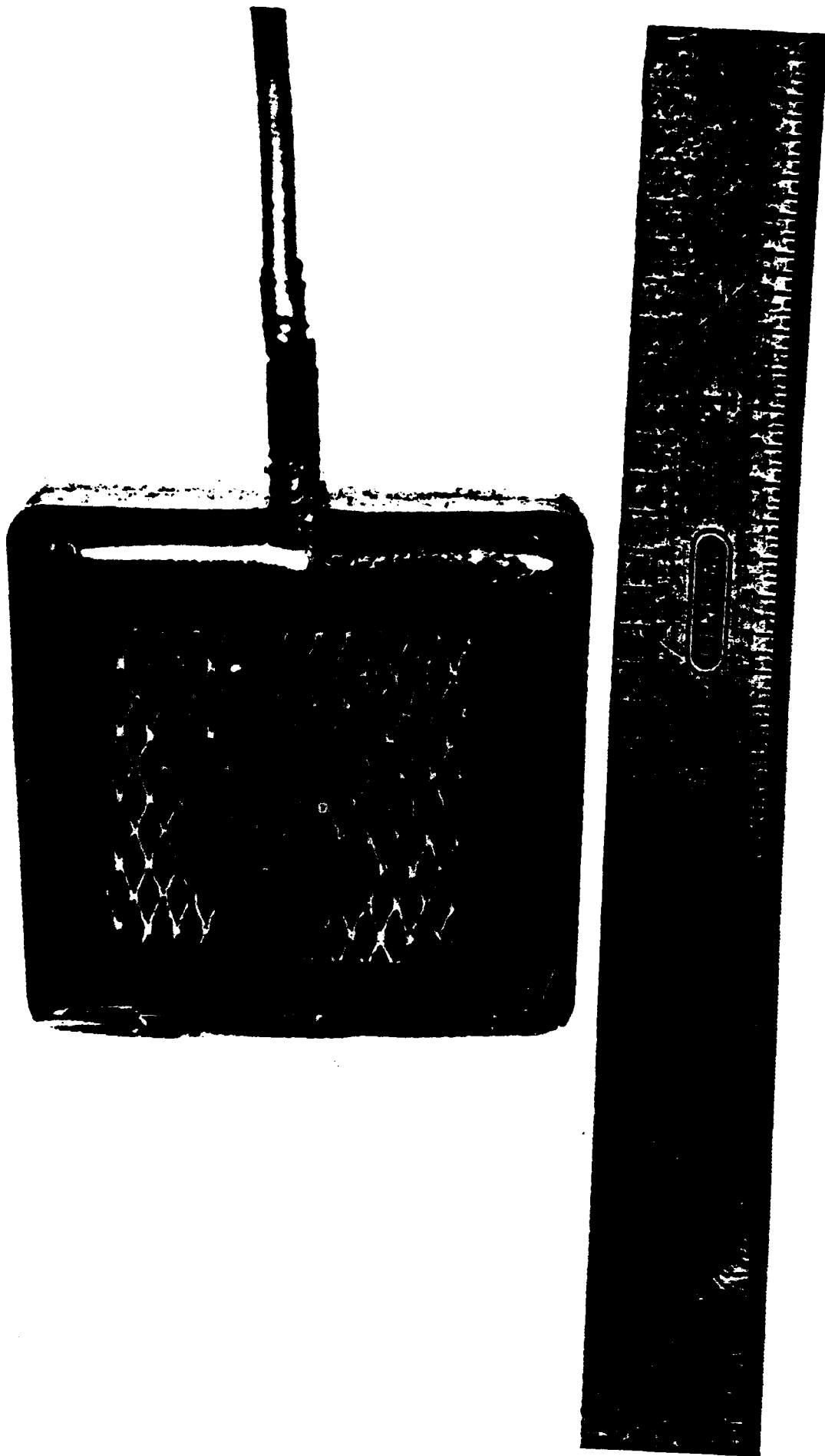


Figure 7. Seven-Layer Copolymer Projector

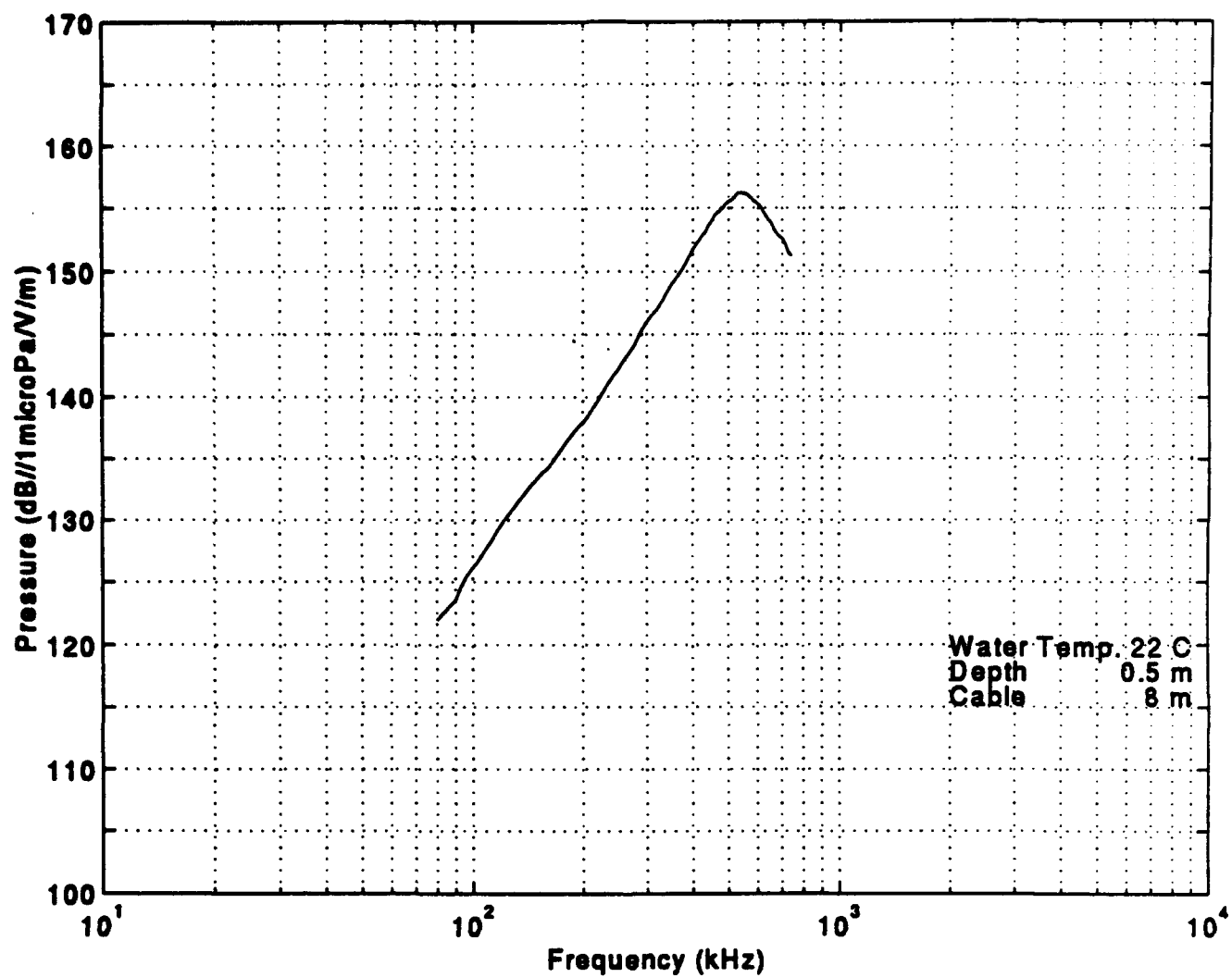


Figure 8. Representative TVR from 80 to 740 kHz of a Seven-Layer Projector (22°C, 0.5 m)

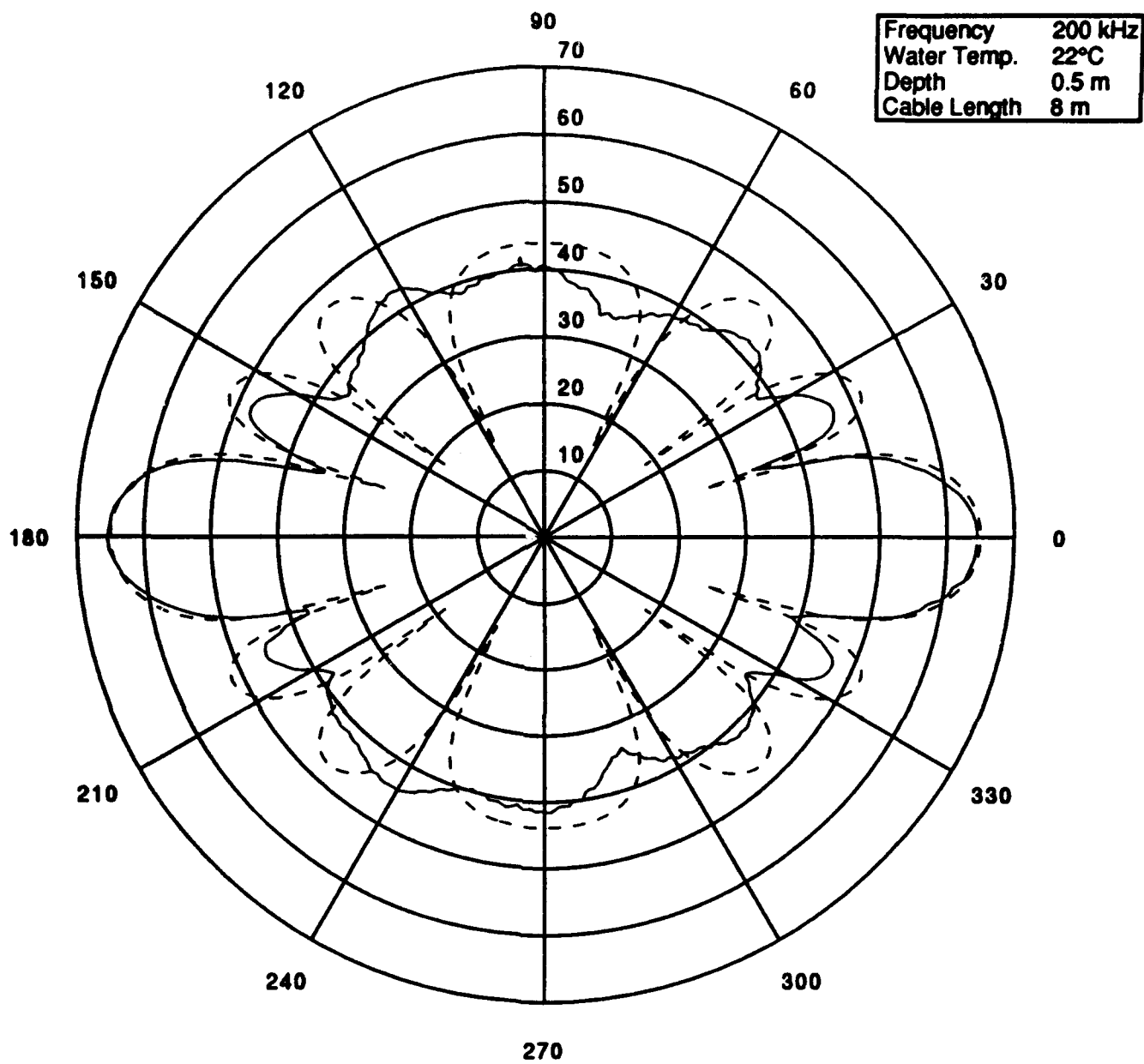


Figure 9. Beam Patterns at 200 kHz (Measured -- Solid Line; Theoretical -- Dashed Line)

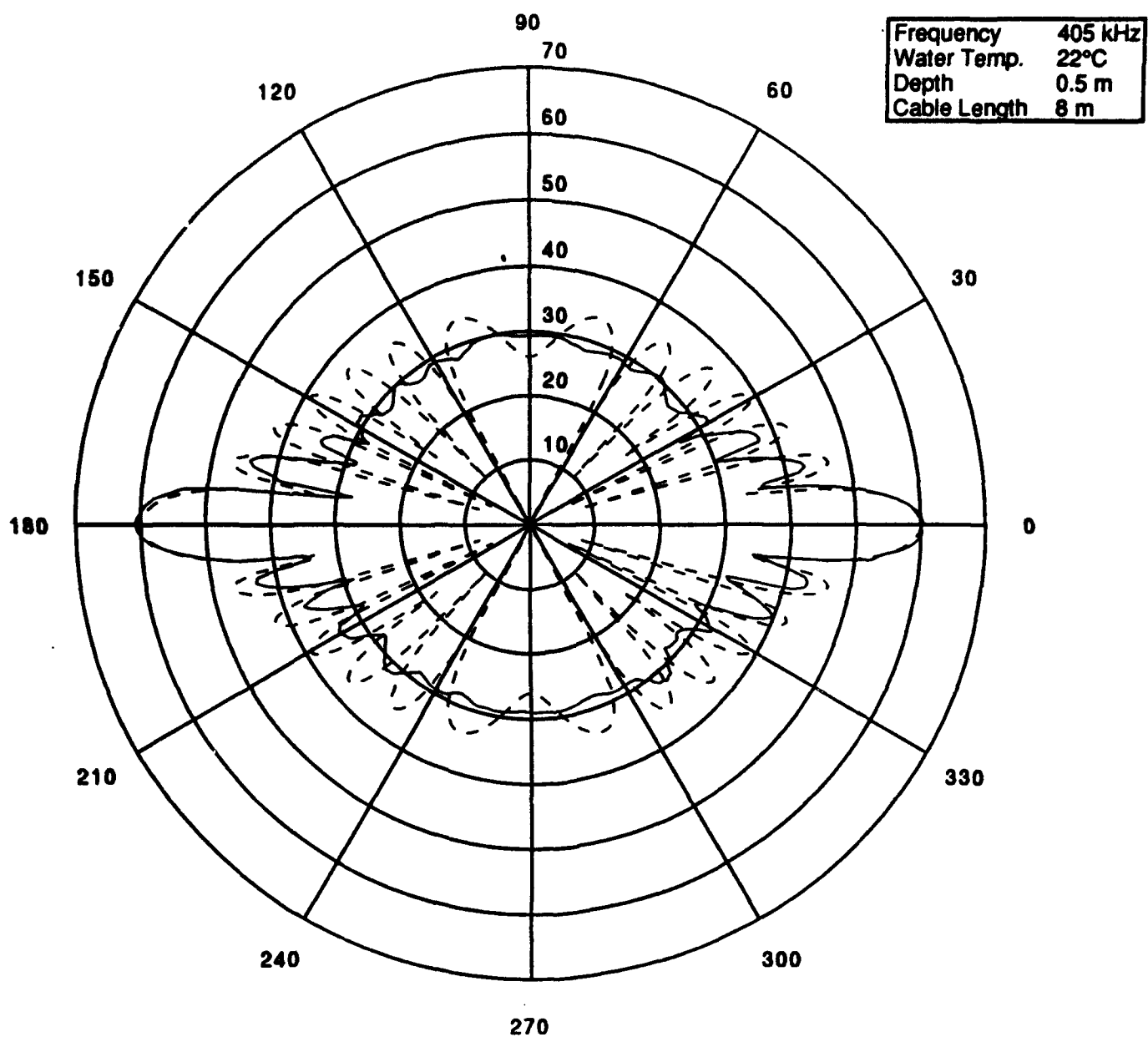


Figure 10. Beam Patterns at 405 kHz (Measured -- Solid Line; Theoretical -- Dashed Line)

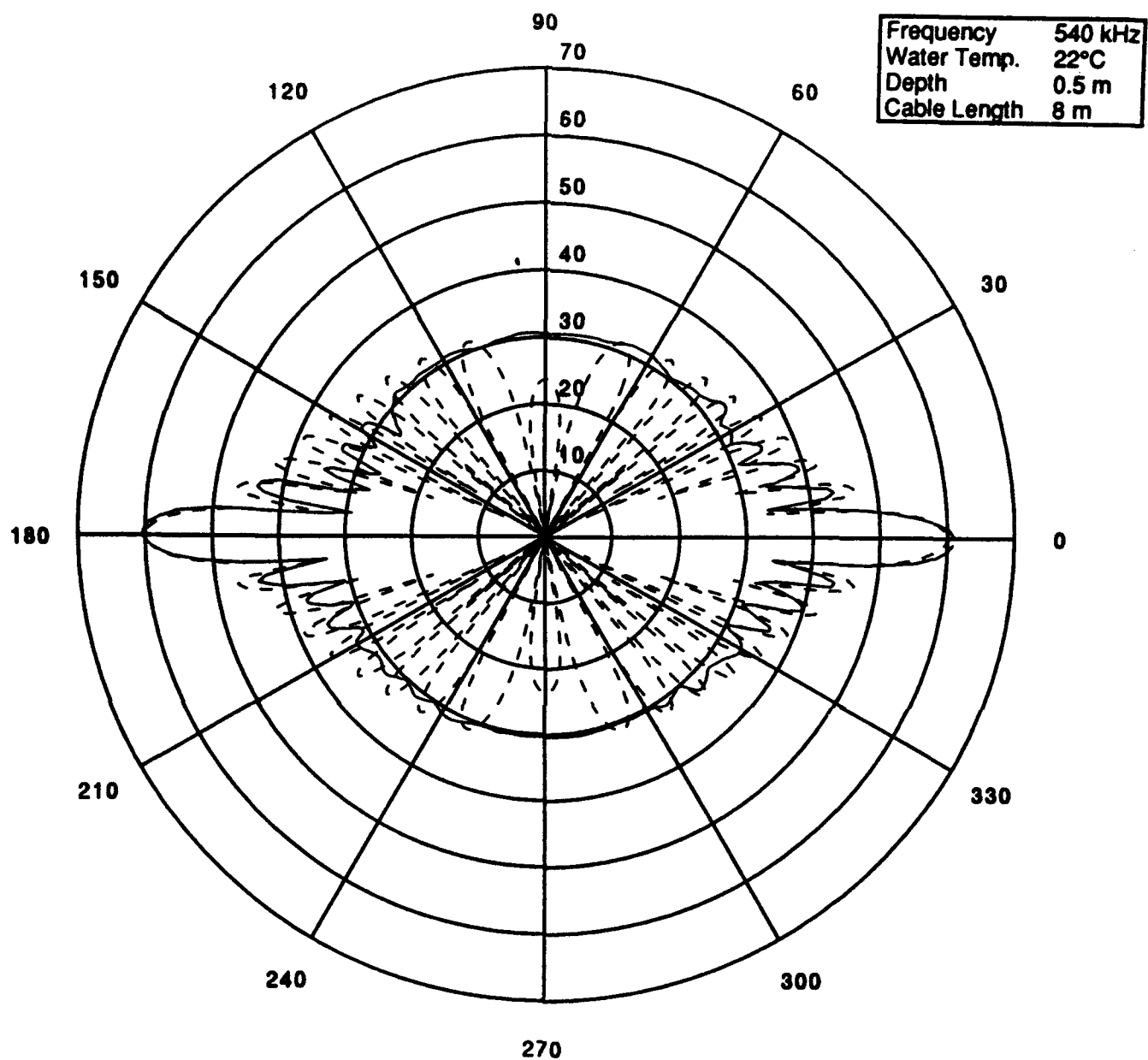


Figure 11. Beam Patterns at 540 kHz (Measured -- Solid Line; Theoretical -- Dashed Line)

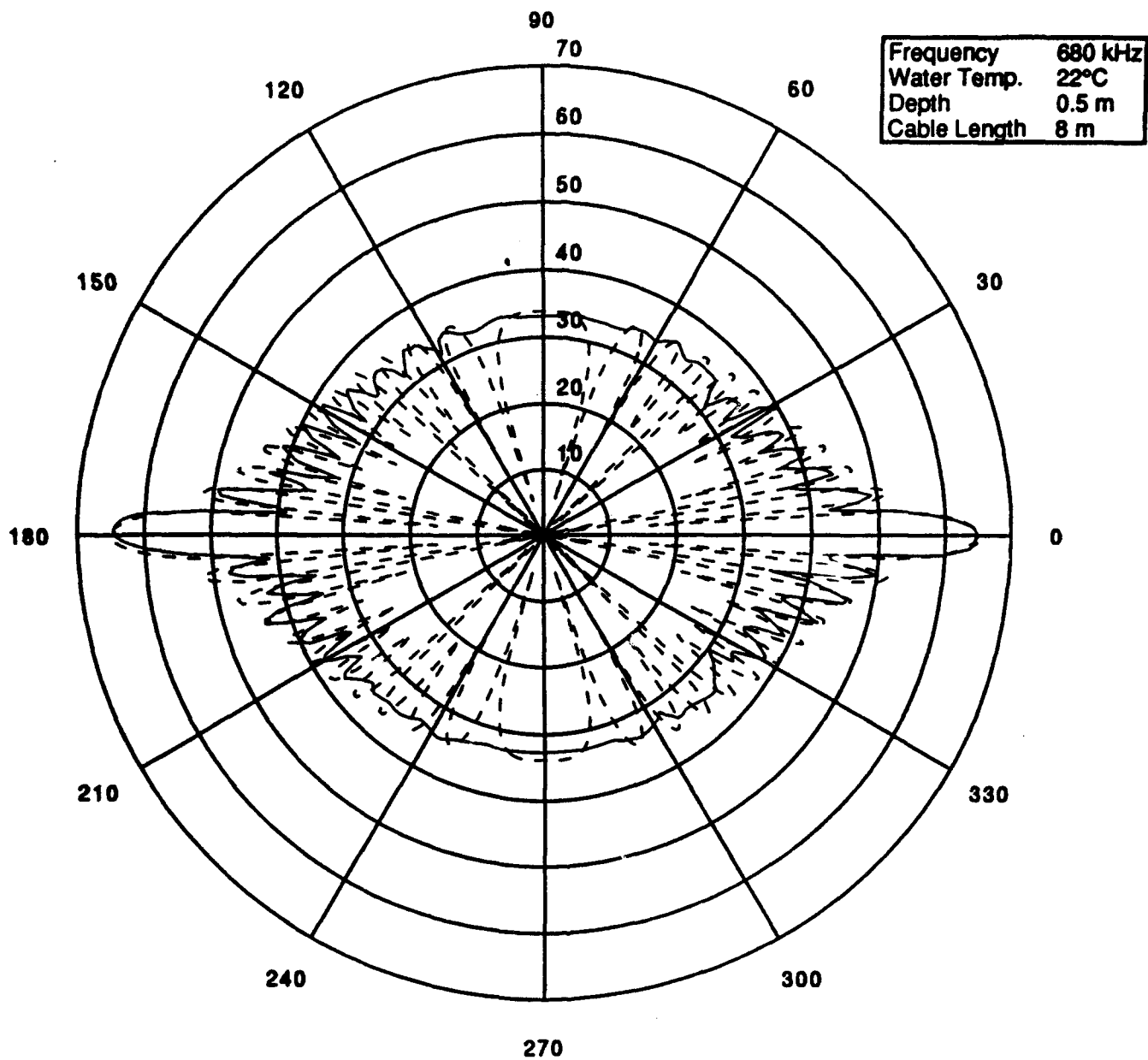


Figure 12. Beam Patterns at 680 kHz (Measured -- Solid Line; Theoretical -- Dashed Line)

Table 1. Properties of Sonar Projector Materials for the 33-Mode

Material	s_{33}^E $\text{m}^2/\text{N} \times 10^{-11}$	d_{33} pC/N	S_{max} $\times 10^{-6}$	$1/2 S_{\text{max}}^2/s_{33}^E$ J/m^3	$k_{33} \%$	$\epsilon_{33}^T/\epsilon_0$	ρ kg/m^3
PZT-4	1.5 ^a	289	160 ^b	842	70	1300 ^a	7500 ^a
PVDF	50 ^c	-25 ^d	750 ^e	563	18 ^f	7 ^c	~1900
75 mol % P(VDF-TrFE) $X_c = 0.75$	30 ^c	-33 ^c	990 ^e	1634	~30 ^f	7.9 ^c	~1900
75 mol % P(VDF-TrFE) $X_c = 0.9$	16 ^g	-34 ^h	893 ^e	2770	--	--	--

^aReference 10

^bAssuming a drive field of 0.557 MV/m.

^cReference 9, table 1.

^dAverage of values from reference 9, table 1.

^eAssuming a drive field of 30 MV/m.

^fReference 2.

^gCalculated value, see text.

^hCalculated with equation (2), assuming that the calculated value is about 50% of the total d_{33} (see reference 9).

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